The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent

Ter Maat, H.; Hogendoorn, J. A.; Versteeg, G. F.

Published in:
Separation and Purification Technology

DOI:
10.1016/j.seppur.2004.10.012

Publication date:
2005

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Separation and Purification Technology 43 (2005) 199–213
Separation Purification Technology
www.elsevier.com/locate/seppur

The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent Part II. The regeneration of copper sulfide to copper oxide—an experimental study

H. ter Maat[a,*], J.A. Hogendoorn[b], G.F. Versteeg[b]

[a] *Procede Group, P.O. Box 328, 7500 AH Enschede, The Netherlands*
[b] *Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received 22 September 2003; received in revised form 11 October 2004; accepted 19 October 2004

Abstract

Aim of this study was to investigate the possibilities for a selective and efficient method to convert copper(II) sulfide (CuS) into copper(II) oxide (CuO). The oxidation of copper sulfide has been studied experimentally using a thermogravimetric analyzer (TGA) at temperatures ranging from 450 to 750 °C and oxygen concentrations of 5 and 10 vol.%. It appeared that the products formed upon the oxidation of copper sulfide depend on the reaction temperature. However, in all cases the conversion time using the powdered samples was much shorter than expected based on literature results (typically 3 min versus 1–3 h as mentioned in literature). The first reaction step in the oxidation of copper sulfide always was the fast decomposition of CuS into Cu_2S and gaseous sulfur, which immediately was oxidized further to SO_2. Subsequently, Cu_2S was then oxidized, the route depending on the reaction conditions. Oxidation experiments carried out at various temperatures showed that Cu_2S was oxidized selectively to CuO at temperatures above 650 °C, while at temperatures below 650 °C (basic) copper sulfate was also formed. The oxidation from Cu_2S to CuO appeared to be the result of two consecutive reactions. Cu_2S is first converted into Cu_2O, which is subsequently oxidized to CuO. The experimental results allowed for the determination of the intrinsic kinetic rate expression and (Arrhenius) relation for the reaction rate constant of the conversion of Cu_2S to Cu_2O between 650 and 750 °C and oxygen concentrations between 5 and 10 vol.%.

Keywords: High temperature oxidation; Copper sulfide oxidation; Reaction mechanism; Thermogravimetric analysis

1. Introduction

Hydrogen sulfide (H_2S) is a component often present in industrial gases. The removal of H_2S from these gases is necessary because of its poisonousness (the MAC value is 10 ppm), and its corrosive and catalyst poisoning properties. Furthermore, the oxidation products of H_2S (SO_2 and SO_3) are considered to be among the main contributants to the so-called acid rain. To purify a gas stream containing H_2S, a host of methods has been developed. Kohl and Nielsen [1] give an extensive review of the hydrogen sulfide removal methods employed nowadays and in the past. The gas stream that has to be desulfurized usually contains other acid components besides H_2S; carbon dioxide (CO_2) being the most common. Co-absorption of these acid components will often take place. This is usually not desired, since it leads to an increase in both the amount of absorbent needed, and in the dimensions of the process equipment. Furthermore, when the desulfurization process is regenerative the co-absorption causes increased energy consumption during regeneration. Since these phenomena do not occur when co-absorption of components other than hydrogen sulfide is avoided, a selective desulfurization of acidic gas streams is an attractive al-

* Corresponding author.
E-mail address: henk.termaat@procede.nl (H. ter Maat).

1383-5866/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2004.10.012

Nomenclature

A	cross-sectional area of the sample cup (m^2)
C	concentration ($mol\,m^{-3}$)
d	characteristic diameter of the sample cup (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
h	height of sample cup (m)
k	mass transfer coefficient ($m\,s^{-1}$)
k	reaction constant ($mol\,kg^{-1}\,s^{-1}$)
m	sample mass (kg)
N	oxygen consumption rate ($mol\,s^{-1}$)
P	pressure (Pa)
R	reaction rate ($mol\,s^{-1}$)
Re	Reynolds number ($\rho v d/\eta$)
Sc	Schmidt number ($\eta/D_{O_2}\rho$)
Sh	Sherwood number ($k_G d/D_{O_2}$)
T	Temperature (K)
v	velocity ($m\,s^{-1}$)

Greek

ε	porosity of the sample bed
η	viscosity (Pa s)
ρ	density ($kg\,m^{-3}$)
ν	stoichiometric coefficient

Superscript

n	reaction order

Subscripts

app	apparent
diff	diffusion
i	inner
o	outer
G	referring to the gas phase
R	denoting reaction
Δ	denoting a difference

ternative to non-selective desulfurization. A selective desulfurization process can be obtained by using an agent that does not utilize an acid–base reaction to remove hydrogen sulfide. A reaction of hydrogen sulfide that is not based on the basic properties of the reagent is a precipitation reaction that occurs when hydrogen sulfide reacts with metal ions present in an aqueous solution. Especially bivalent metal ions are suitable for this application since the solubility of the sulfides of these metals is usually very low. When a bivalent metal ion and hydrogen sulfide are brought in contact with each other the following overall precipitation reaction can take place if the solubility product of the metal sulfide is exceeded.

$$Me^{2+} + H_2S + 2H_2O \leftrightarrow MeS\downarrow + 2H_3O^+ \quad (1)$$

A selective absorbent, i.e. an absorbent that does not react with carbon dioxide, can be obtained when the metal ion and process conditions are chosen such that the precipitation of the corresponding metal carbonate does not occur. Investigations on the reaction of H_2S and CO_2 with aqueous metal sulfate solutions [1,2] have shown that a copper sulfate solution is a suitable choice for such a selective desulfurization process. Procede Twente has patented a new regenerative gas desulfurization process based on this precipitation reaction [3,4]. A simplified scheme of the process under development is shown in Fig. 1. In this process the gas stream contaminated with hydrogen sulfide is brought in contact with the washing liquor in a gas liquid contactor, the absorber. In the absorber H_2S reacts with the aqueous $CuSO_4$ solution under the formation of solid CuS and an aqueous solution of sulfuric acid. The now desulfurized gas stream is available for further processing. The precipitates in the acidic copper sulfate solution that leaves the absorber are removed from the absorbent stream in a liquid-solid separator. The now solids-free solution is brought to a dissolver. In the dissolver a make up stream of solid CuO is added to the acidic $CuSO_4$ solution. In the dissolver CuO reacts according to

$$CuO + 2H_3O^+ + {SO_4}^{2-} \leftrightarrow Cu^{2+} + 3H_2O + {SO_4}^{2-} \quad (2)$$

By dissolving CuO in the acidic $CuSO_4$ solution both the acidity generated in the scrubbing step is neutralized and the scrubbing solution (Cu^{2+}) is replenished. Also a relatively small amount of water will be formed. Thus, by adding solid CuO instead of e.g. solid $CuSO_4$ the need for adding an additional neutralizing agent is omitted. Summarizing it can be concluded that the absorption section of the desulfurization process consumes CuO and produces CuS and a treated, clean gas stream. This process step can function as a stand alone unit, but for economic reasons it is preferred to avoid the external purchase of CuO and to regenerate the produced solid CuS in the desulfurization process itself. A regeneration step complementary to the absorption step can be created by the oxidation of CuS to CuO. During this process step the sulfur bound by the copper will be released as SO_2, which can easily be oxidized to SO_3, which in turn can be used for the production of concentrated sulfuric acid. The object of the current investigation is to illuminate the reactions that can occur during the oxidation of copper sulfide, the products formed and the rate at which these reactions occur. The results can then be used to enable an optimal design of an oxidizing process for the regeneration of copper sulfide.

2. Literature

The oxidation reactions of copper sulfide are of importance in the refining of ore containing natural occurring copper sulfides, or copper–iron sulfide. Therefore, the subject has been studied frequently. Peretti [5] developed a method to study the reactions that occur during the roasting of CuS. Peretti [5] found that CuS is first converted into Cu_2S under the release of (gaseous) sulfur. The formed Cu_2S is then oxi-

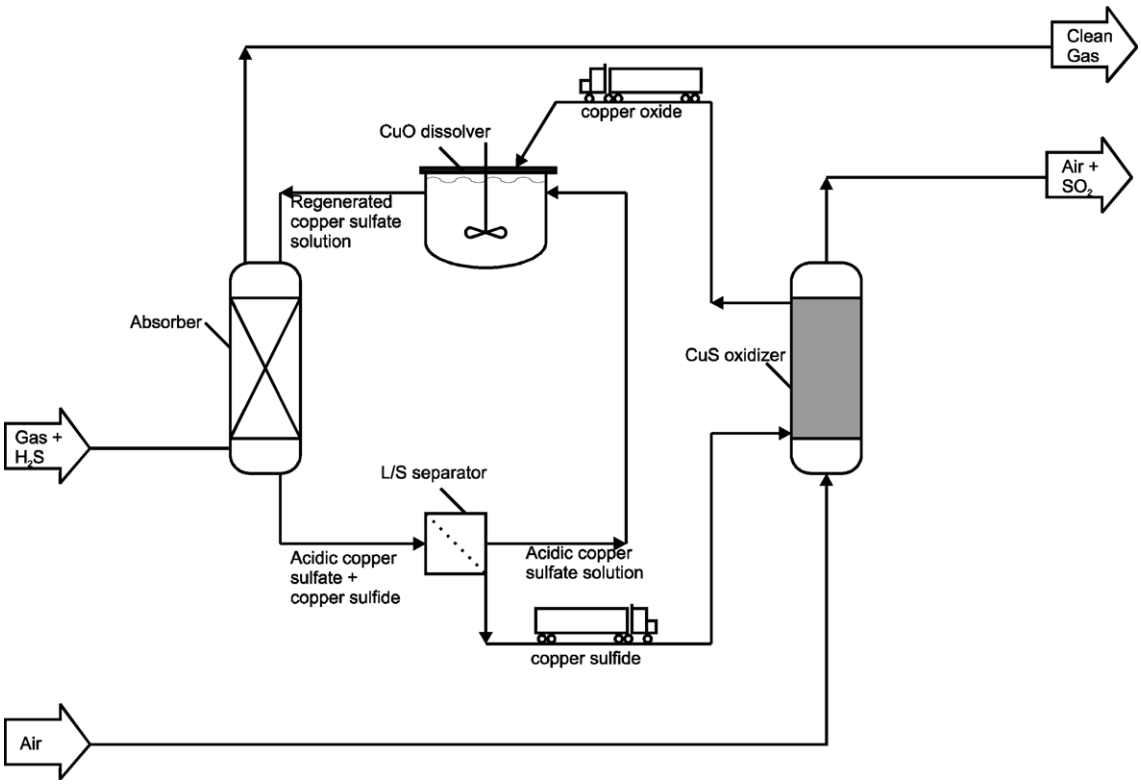

Fig. 1. Process scheme of the Procede gas desulfurization process.

dized into Cu_2O, which is subsequently converted into CuO. At temperatures above 663 °C CuO was the only observed final product; at temperatures below 663 °C copper sulfate was also found. At temperatures below 500 °C the reaction nearly ceased after a certain period of time.

Lewis et al. [6] have studied the oxidation of powdered Cu_2S (with a particle size between 0.149 and 0.074 mm) in both air and in pure oxygen at temperatures between 250 and 700 °C. The main interest was to determine the amount of water soluble and acid soluble copper components formed. Lewis et al. [6] found the optimum temperature for the formation of water soluble copper components ($CuSO_4$) to be 450 °C, when using air or oxygen as reaction gas. At a temperature of 700 °C a complete conversion to acid soluble copper substances (CuO, $CuO{\cdot}CuSO_4$ and $CuSO_4$) was found to be possible in 60 min when using air as oxidizing agent. When using pure oxygen as oxidizing agent only 8% of the Cu_2S was converted into water soluble copper components. The remainder of the copper was present as acid soluble copper components. Ganguly and Mukherjee [7] have studied the oxidation of CuS in a fixed bed in a nitrogen/oxygen atmosphere at temperatures varying between 340 and 410 °C. Ganguly and Mukherjee [7] found that the main solid product formed during the oxidation reaction was cuprous oxide (Cu_2O). Besides cuprous oxide small amounts of cupric oxide (CuO) and $CuSO_4$ were formed. Ganguly and Mukherjee [7] also found indications that the first step in the overall reaction was the decomposition of CuS to Cu_2S and elemental sulfur. The formed elemental sulfur is, in the presence of oxygen, immediately oxidized to sulfur dioxide. No reaction was observed when the temperature was below 340 °C. The amount of $CuSO_4$ formed increased with increasing temperature. Only a negligible amount of CuO was found at the temperatures used. Ramakrishna and Abraham [8] have studied the rate of the reactions that occur during the roasting of Cu_2S at temperatures between 750 and 950 °C. Açma et al. [9] studied the roasting of iron ore concentrates containing small amounts of Cu_2S, CuS and $CuFeS_2$ and other metal sulfides in a rotary furnace. The object of that study was to determine the experimental conditions for the conversion of the non-ferro metal sulfides to compounds soluble in water or acidic aqueous solutions. It was found that the copper sulfides were converted mainly to basic copper sulfate ($CuO{\cdot}CuSO_4$) in an atmosphere containing approximately 13 vol.% SO_2, and 4 vol.% oxygen (a typical roast gas composition found in the process used to process the ore concentrates). The optimal roasting temperature for conversion towards soluble copper components was found to be 690 °C. Their experimental results show that the formation of $CuSO_4$ and $CuO{\cdot}CuSO_4$ is possible if the experimental conditions and the reaction times allow the formation of these components even at temperatures as high as 690 °C. The oxidation of a pellet of Cu_2S at atmospheric pressure, various temperatures and oxygen concentrations has been studied by Asaki et al. [10]. The reaction temperature was varied between 750 and 850 °C. The oxygen concentration was varied between 5 and 20 vol.%. The

diameter of the pellets used was approximately 6 mm. The oxidation of Cu_2S appeared to be a two stage process. First Cu_2S was oxidized to Cu_2O, which was then oxidized further to CuO. This hypothesis was supported by the intersection of a partly oxidized pellet. This pellet showed a layered structure; the core was found to be unconverted Cu_2S, the inner layer was Cu_2O, and the outer layer consisted of CuO. Under the experimental conditions the gas phase mass transfer resistance initially determined the rate of the reaction. As the reaction proceeded, diffusion through the product layer was assumed to become rate determining. Except for one experiment carried out at 750 °C copper sulfate was not formed. At a temperature of 850 °C the pellets melted partly due to the exothermic reaction. The time needed to completely convert a single pellet of Cu_2S to CuO was approximately 3 h.

3. Thermodynamics

In Fig. 2, a phase diagram of the Cu–S–O system is shown as a function of the partial pressure of SO_2 and O_2 at a temperature of 727 °C. This diagram has been composed using the thermodynamic data given by Barin [11]. This diagram indicates that at a temperature of 727 °C CuO is the most stable component when a Cu–sulfur component is brought in contact with a gas mixture with a partial pressure of SO_2 less than 10^{-2} bar and a partial pressure of O_2 more than 10^{-4} bar. In order to establish the possible gas solid reactions during the oxidation of copper sulfide the changes in Gibbs free energy accompanying these reactions were calculated at temperatures ranging from 227 to 727 °C using the data compiled by Barin [11]. The partial pressure of O_2 and SO_2 used in these calculations was 10^{-1} and 10^{-6} bar, respectively. The temperature range and the partial pressure of O_2 for which these calculations were performed are corresponding with the temperature range and partial pressure of O_2 at which the current copper sulfide oxidation experiments were carried out. An overview of the gas solid reactions that can possibly occur and the Gibbs free energy that accompanies these reactions is given in Table 1. From Table 1, it can be seen that it is possible to convert copper sulfide (CuS or Cu_2S) directly or indirectly into copper oxide (CuO or Cu_2O), $CuSO_4$ or basic copper sulfate ($CuO{\cdot}CuSO_4$). At temperatures below 527 °C the conversion of $CuSO_4$ into $CuO{\cdot}CuSO_4$ is possible, but $CuO{\cdot}CuSO_4$ itself is a stable component, even at SO_2 vapor pressures as low as 10^{-6} bar. At temperatures above 527 °C the conversion of $CuO{\cdot}CuSO_4$ into the desired end product CuO becomes possible if the SO_2 vapor pressure is lower than the equilibrium pressure. The phase diagram given in Fig. 3 illustrates the relation between the temperature, the partial pressures O_2 and SO_2 and the stable component in the Cu–S–O system. To avoid excessive costs associated with the further processing of the produced SO_2 to H_2SO_4 in an industrial process a concentration of SO_2 in the oxidizer off gas of at least 3 vol.% should be maintained [12]. Furthermore, the presence of (basic) copper sulfate in the product of the oxi-

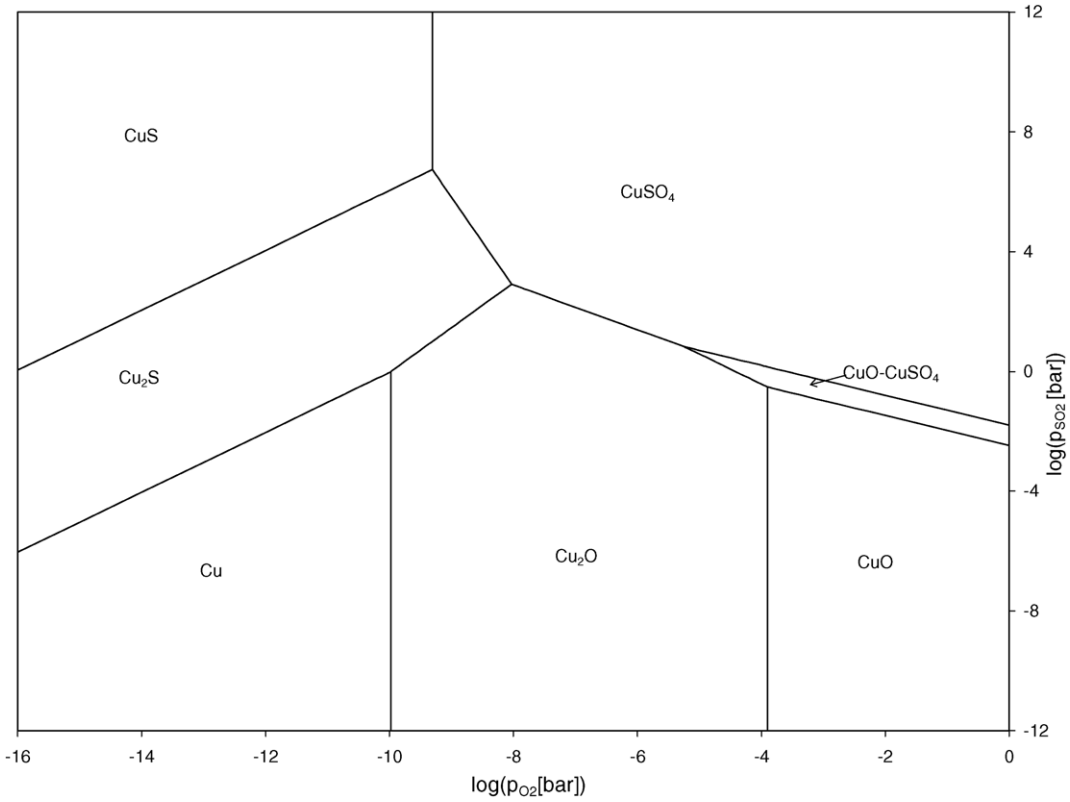

Fig. 2. Phase diagram of the Cu–S–O system at a temperature of 727 °C.

Table 1
Possible reactions and Gibbs free energy accompanying these reactions at various temperatures and at $P_{SO_2} = 10^{-6}$ bar, $P_{S_2} = 10^{-3}$ bar and $P_{O_2} = 10^{-1}$ bar [11]

Equation	Reaction (stoichiometry)	ΔG (kJ/mol product)			
		227 °C	427 °C	627 °C	727 °C
(3)	$2CuS \rightarrow Cu_2S + \frac{1}{2}S_2$	10	−24	−59	−75
(4)	$S_2 + 2O_2 \rightarrow 2SO_2$	−344	−337	−330	−326
(5)	$2CuS + O_2 \rightarrow Cu_2S + SO_2$	−334	−361	−390	−402
(6)	$CuS + 2O_2 \rightarrow CuSO_4$	−515	−435	−356	−318
(7)	$Cu_2S + 3O_2 + SO_2 \rightarrow 2Cu$	−697	−509	−323	−233
(8)	$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2$	−385	−381	−374	−372
(9)	$Cu_2S+O_2 \rightarrow 2Cu + SO_2$	−258	−270	−280	−286
(10)	$Cu_2O + \frac{3}{2}O_2 + 2SO_2 \rightarrow 2CuSO_4$	−311	−129	51	139
(11)	$Cu_2O + \frac{1}{2}O_2 \rightarrow 2CuO$	−82	−60	−38	−28
(12)	$2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O$	−128	−111	−94	−86
(13)	$2CuSO_4 \rightarrow CuO \cdot CuSO_4 + \frac{1}{2}O_2 + SO_2$	111	30	−50	−90
(14)	$CuO \cdot SO_4 \rightarrow 2CuO + \frac{1}{2}O_2 + SO_2$	118	39	−39	−77
(15)	$Cu_2O + \frac{1}{2}O_2 + SO_2 \rightarrow CuO \cdot CuSO_4$	−200	−99	1	49

dizer is not desired since it does not (or to a lesser extent) act as a base in the make up section of the process scheme depicted in Fig. 1, and should therefore be avoided. Given the relatively low equilibrium partial pressure of SO_2, the decomposition of basic copper sulfide $CuO{\cdot}CuSO_4$ into CuO will not take place below 727 °C if the reaction gas contains a significant amount of SO_2 (see Fig. 3). At a temperature of 727 °C the decomposition of $CuO{\cdot}CuSO_4$ into CuO may take place if the amount of SO_2 does not exceed 1 vol.% at atmospheric pressure (note that this percentage is slightly lower than the desired minimal concentration of 3%). Thus, starting from $CuO{\cdot}CuSO_4$ a (basic) copper sulfate free product can only be obtained at a temperature well above 727 °C. However, operating an oxidizer at very high temperatures is not desired

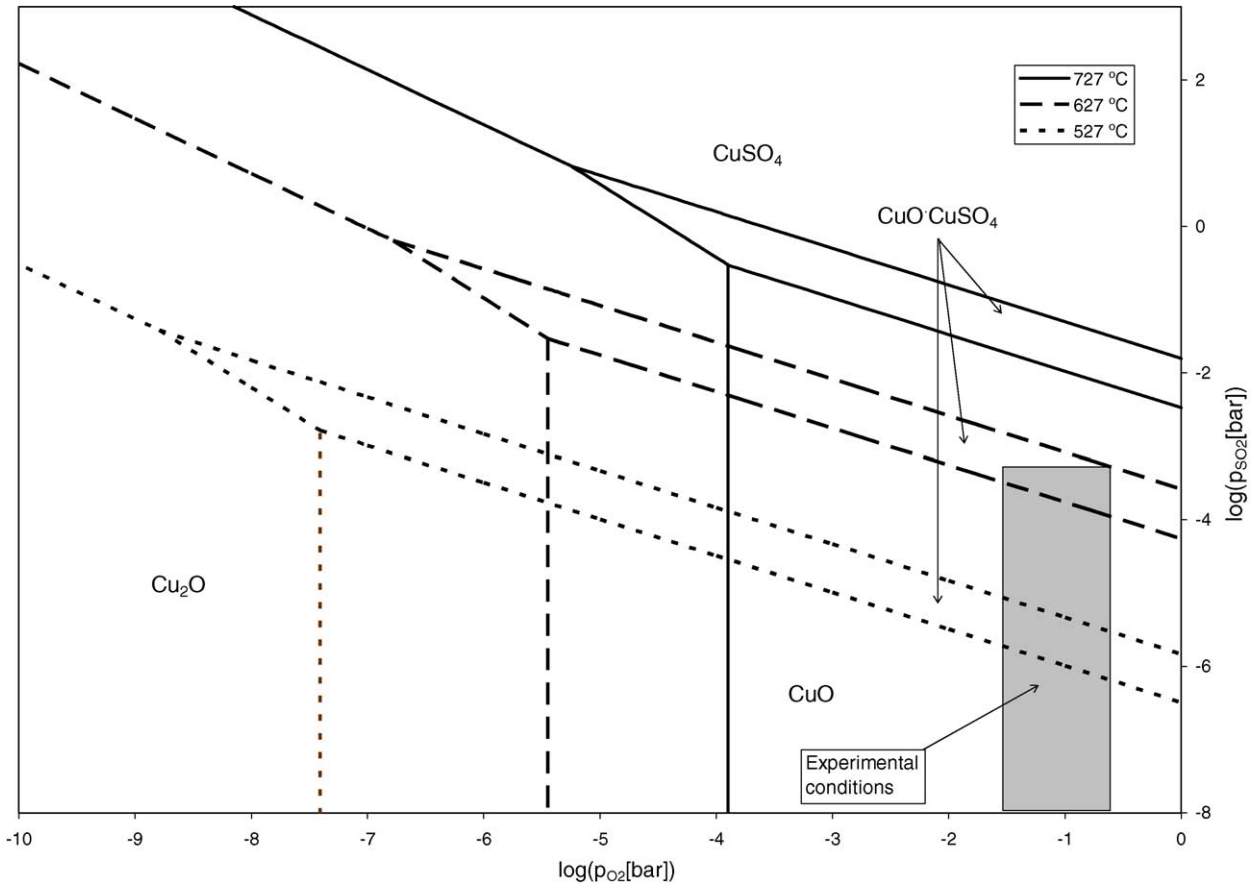

Fig. 3. Detail of the phase diagram of the Cu–S–O system at temperatures, oxygen and sulfur dioxide vapor pressures relevant to the experiments.

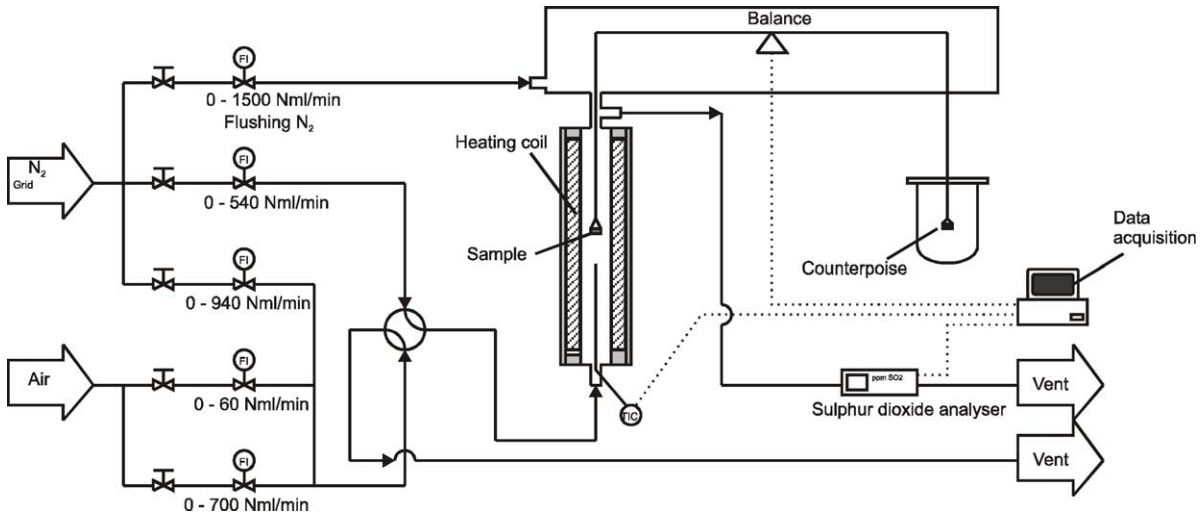

Fig. 4. Schematical representation of the thermogravimetric analyzer.

since it is known, from the experiments performed by Açma et al. [9], that the copper oxide produced at high temperatures (i.e. above 700 °C) does not completely dissolve in an acidic solution. Açma et al. [9] also found that the amount of copper oxide that does not dissolve increases with the reaction temperature. An explanation for this behaviour may be found in the sintering or even the partial melting of the copper sulfide at very high temperatures, an effect also noted by Asaki et al. [10] at temperatures of 850 °C. To avoid both the presence of (basic) copper sulfate and insoluble compounds in the end product a method is needed to convert CuS selectively in CuO at the lowest possible temperature without the production of $CuSO_4$ or $CuO{\cdot}CuSO_4$ as intermediate products. It is thus desirable to convert the copper sulfide selectively and completely into CuO. Therefore, this experimental study will be focused not only on the determination of the overall reaction rate of the oxidation of copper sulfide, but will also try to establish the influence of the reaction conditions (e.g. temperature and oxygen concentration) on the reaction path of the oxidation of copper sulfide. This will allow the determination of the optimal reaction conditions in an industrial oxidizer.

4. Experimental set-up and procedure

The experiments have been performed in a thermogravimetric analyser (TGA). The experimental set-up is schematically shown in Fig. 4. The experimental set-up can be subdivided in three sections: a gas mixing section to prepare the desired gas mixture, a reactor section (the TGA), and a gas analysis section. The reactor section of the TGA consists of two concentrically placed quartz glass tubes. In the annular space between the tubes a heating coil is present. The reactor module was thoroughly insulated. The temperature in the reactor was measured using two K-type thermocouples and controlled by an Eurotherm 91^e type controller. A small sample was brought in the reactor on a small quartz cup that was attached to one end of the lever of a Sartorius 4406 microbalance by means of a small platinum hook. The dimensions of the quartz cups are given in Fig. 5 and Table 2. A counterpoise was attached to the other end of the lever. The mass of the counterpoise could be altered to match the weight of the sample plus the quartz cup. To avoid corrosion of the microbalance by the sulfur dioxide released during the course of the oxidation reaction, the upper section of the microbalance was continuously flushed with a stream of ni-

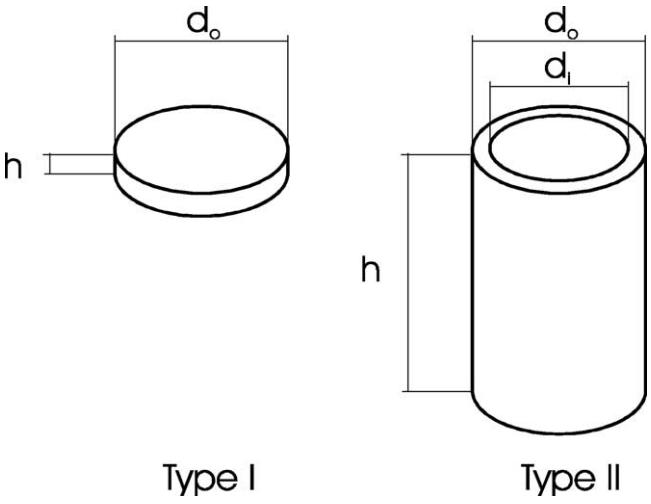

Fig. 5. Quartz cups used.

Table 2
Dimensions of the cups used

	Cup type I	Cup type II
h ($\times 10^{-3}$ m)	2	8.5
d_o ($\times 10^{-3}$ m)	4.5	7
d_i ($\times 10^{-3}$)		4.0

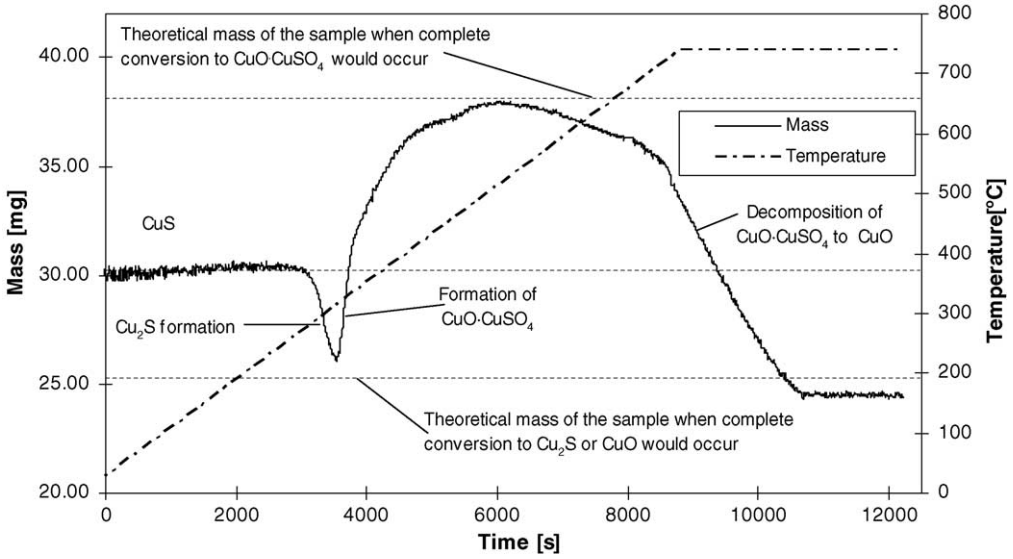

Fig. 6. Exploratory TGA experiment, using 30 mg CuS as starting material, the sample heating rate was 5 °C/min, the gas flow rate through the reactor was 11.6 N ml s^{-1} and the gas entering the reactor contained 21 vol.% oxygen. The horizontal dotted lines show the weight that the sample would have if all copper in the sample would be converted into $CuO{\cdot}CuSO_4$ (top line), CuS (middle dotted line) or Cu_2S or CuO (bottom line).

trogen. A Brooks R-2-15-A flowmeter was used to control this flow. The reaction gas entered the reactor via the bottom. A four-way valve was used to select if a stream of pure nitrogen or a mixture of nitrogen and air entered the reactor. Brooks E 5850 TR mass flow controllers were used to control the flow of the pure nitrogen stream (which could be varied between 60 and 540 N ml min^{-1}) and the flow rate and composition of the mixture of nitrogen and air (the flow rate of the mixture was chosen to be identical to the flow rate of the nitrogen stream, while the oxygen content could be varied between 2.0 and 21.0 vol.%). The sulfur dioxide content of the gas that left the reactor was continuously monitored using a MAIHAK UNOR 610 infrared sulfur dioxide analyzer. Unless stated otherwise, the following experimental procedure was applied. The selected quartz glass cup was filled with a sample of copper sulfide of a precisely known weight varying between 1 and 32 mg. The cup was then attached to the platinum hook in the TGA oven. The oven was then flushed continuously with pure nitrogen and was heated to a preset temperature at a rate of 15 °C/min. When the desired temperature was reached the four-way valve was switched and the air/nitrogen mixture was allowed to enter the reactor, starting the reaction. During the experiment the weight of the sample, the sulfur dioxide concentration in the gas leaving the reactor and the temperature of the reactor were recorded. During a number of experiments the air/nitrogen mixture was fed to the reactor during the temperature ramp. Sieve fractions of reagent grade copper sulfide (Cu_2S) and reagent grade copper sulfide (CuS) (−100 mesh) were used during the experiments. The Cu_2S (originally −325 mesh) was sieved using 32, 38, and 45 μm sieves.

Copper(I) sulfide (Cu_2S) and copper(II) sulfide (CuS) of 98%, respectively, +99% purity were obtained from Aldrich. Nitrogen and synthetic air were obtained from Hoek Loos. The nitrogen was of 99.9% purity and the composition of the air was 21% oxygen and 79% nitrogen. The calibration gas for the IR analyzer was prepared by Praxair and had a calibrated composition of 424 ppm $SO_2 \pm 9$ ppm. The gross composition of the sample could be determined from the mass balances. The remaining sulfur content of the sample was determined using the data gathered by the IR and the effluent gas flow rate. The oxygen content of the sample could subsequently be determined from the total mass of the sample as measured by the microbalance and the mass of sulfur in it as determined from the integrated results of the IR. The gross composition of the sample could be used to determine the (relative) amounts of the components present in the sample during the experiment. As a check of the sulfur mass balance the total amount of sulfur dioxide emitted by the sample was used. On average the total amount of sulfur brought into the reactor as Cu_2S matched the amount leaving the reactor as determined by the sulfur dioxide analyzer within 10%. As a check on the total mass balance, the mass of the completely reacted sample was compared with the original mass of the unreacted sample. Since the molar masses of the reagent (Cu_2S) and the desired end product (CuO) are known the mass that the sample should have at the end of an experiment can be calculated.

5. Results

5.1. Reaction path and stoichiometry

An exploratory study into the reaction path of the oxidation of copper sulfide was carried out by performing exper-

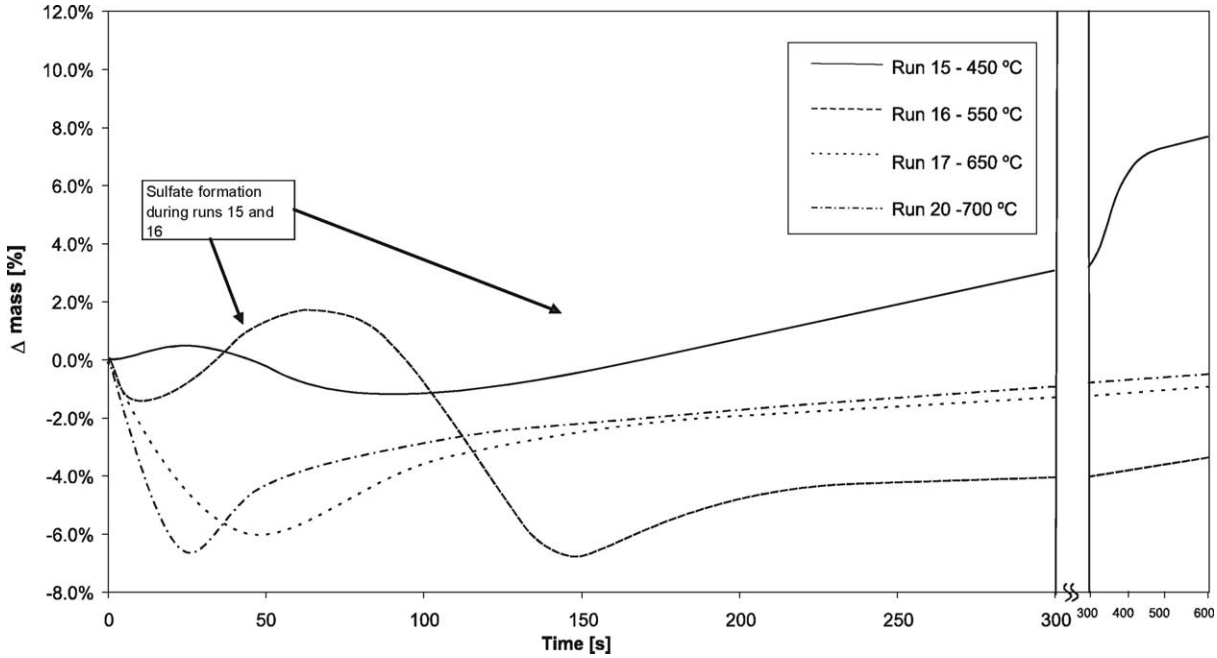

Fig. 7. Mass of the sample as a function of time for various temperatures (runs 15–21).The temperature was varied between 450 and 725 °C. The concentration of oxygen in the feed gas was 10 vol.%. The initial sample mass was approximately 1 mg.

iments using the TGA. A copper sulfide sample of a known weight was brought in the TGA and was gradually heated to a temperature of 740 °C in an oxygen containing atmosphere. The intermediate products formed during the oxidation of copper sulfide were analyzed using the method described by Ganguly and Mukherjee [7]. Fig. 6 represents the mass of the sample and the temperature in the TGA during the experiment. From Fig. 6, it can be seen that the conversion of CuS into Cu_2S starts to take place at a relatively low temperature of approximately 300 °C. CuS decomposes into Cu_2S and elemental sulfur according to Eq. (3) (listed in Table 1). The gaseous elemental sulfur (S_x) that is liberated during this step is oxidized into sulfur dioxide (Eq. (4)) when it comes into contact with the oxygen from the gas surrounding the

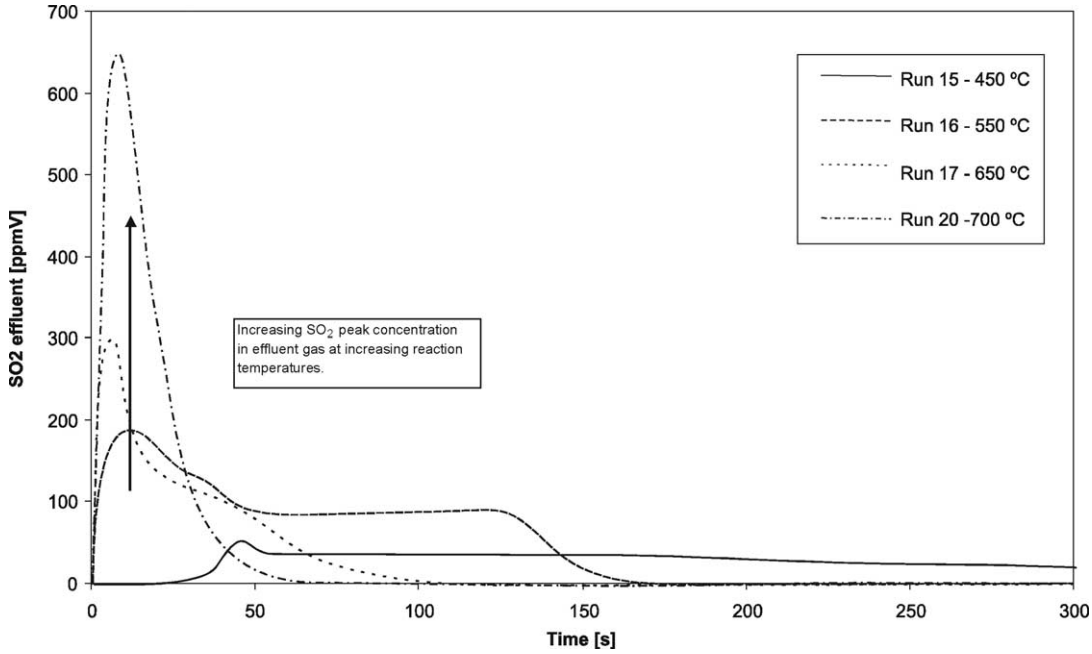

Fig. 8. The sulfur dioxide concentration in the effluent gas as a function of time for various temperatures (runs 15–21). The temperature was varied between 450 and 725 °C. The concentration of oxygen in the feed gas was 10 vol.%. The initial sample mass was approximately 1 mg.

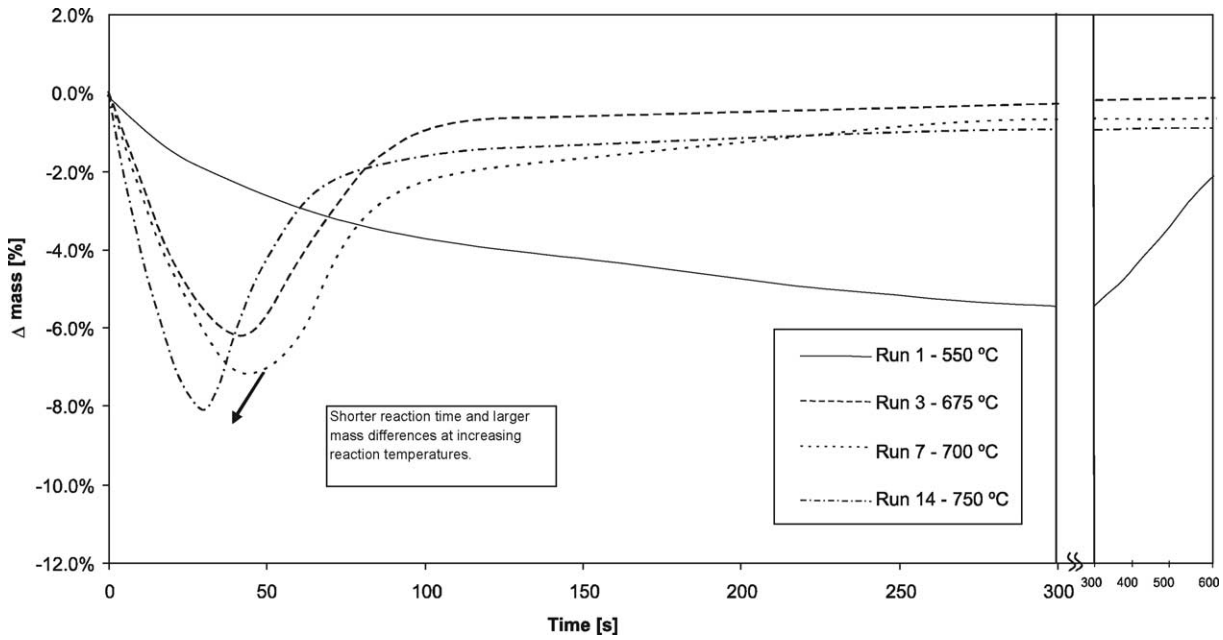

Fig. 9. Mass of the sample as a function of time for various temperatures (runs 1–14). The temperature was varied between 550 and 725 °C. The concentration of oxygen in the feed gas was 5 vol.%. The initial sample mass was approximately 1 mg.

sample. Only when the conversion of CuS towards Cu_2S is completed, Cu_2S is oxidized further to $CuO{\cdot}CuSO_4$. As can be seen in Fig. 3 $CuO{\cdot}CuSO_4$ is an unstable component at temperatures above 527 °C, but only at temperatures above approximately 650 °C the decomposition of $CuO{\cdot}CuSO_4$ actually takes place at a rate that is accurately measurable with the experimental set-up used in the present study.

5.2. Oxidation of Cu_2S

In order to find a possible reaction route of CuS to CuO the oxidation of copper sulfide at temperatures up to 750 °C has been studied in detail experimentally. CuS very rapidly decomposes into Cu_2S and gaseous sulfur at temperatures above 300 °C, both in the presence and absence of O_2 [5,7]

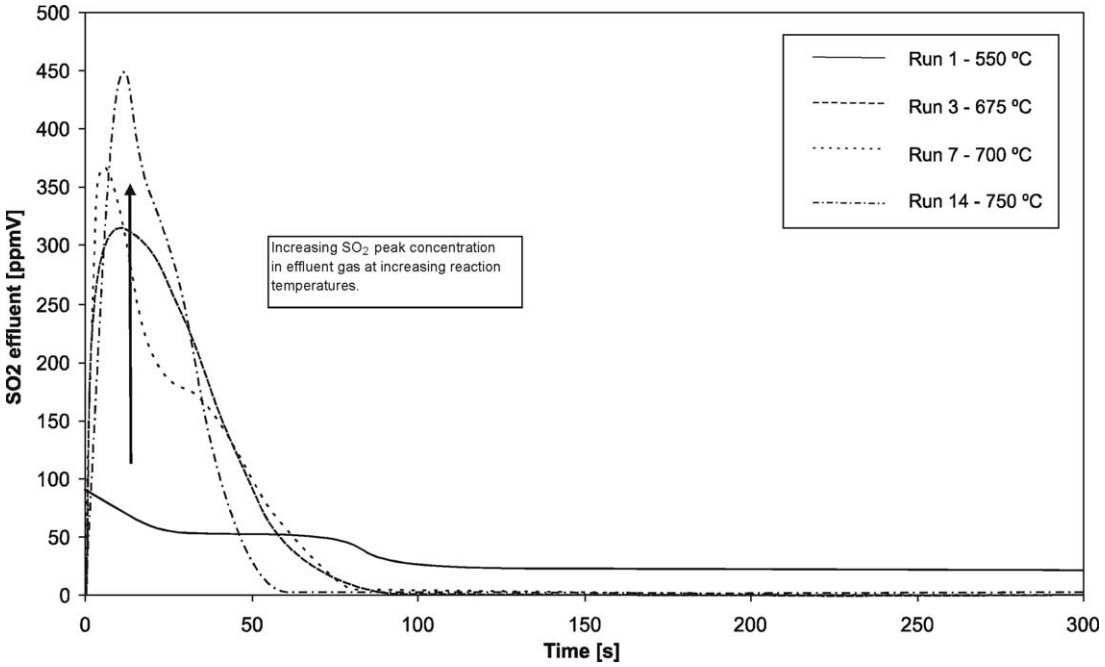

Fig. 10. The sulfur dioxide concentration in the effluent gas as a function of time for various temperatures (runs 1–14). The temperature was varied between 550 and 725 °C. The concentration of oxygen in the feed gas was 5 vol.%. The initial sample mass was approximately 1 mg.

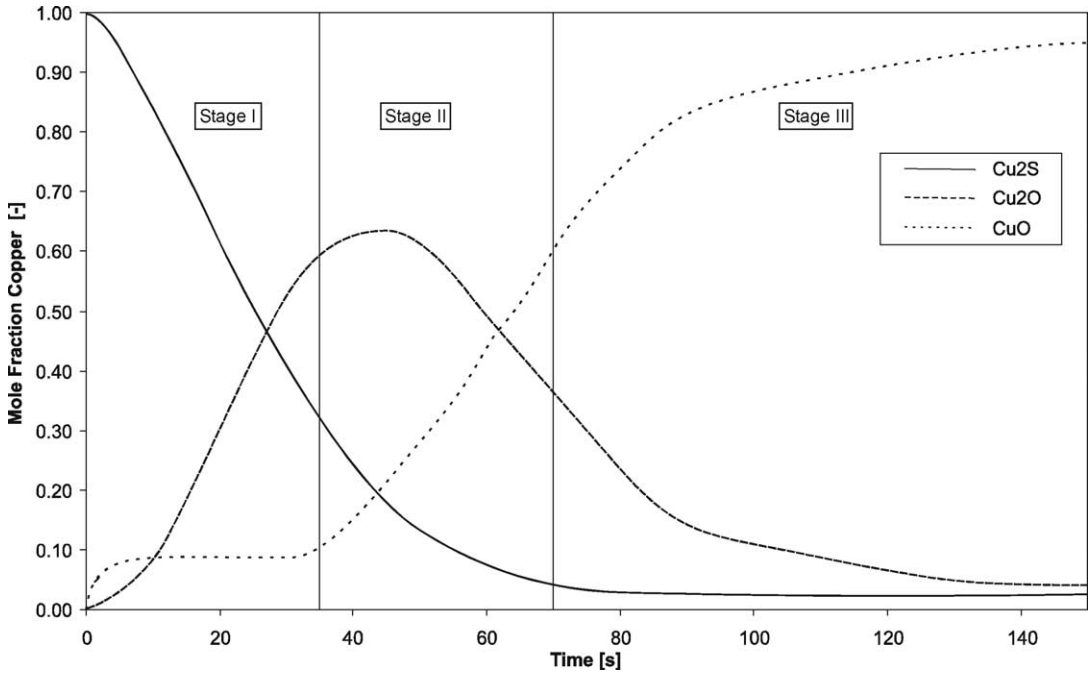

Fig. 11. Various components formed as a function of time during run 3. These results represent the typical behaviour for Cu_2S samples for temperatures above 550 °C. The boundary between stages I and II is chosen so that the maximum amount of CuO present in the sample during stage I was 10%. The boundary between stages II and III is chosen so that the maximum amount of Cu_2S present in the sample during stage III was 10%.

and Appendix A. Therefore, the current oxidation experiments were further performed with Cu_2S (always being the first product of the decomposition reaction of CuS) as reactant. During the experiments performed to study the oxidation of Cu_2S a number of parameters was varied systematically; the diameter of the sample particles, the reactor temperature, the amount of sample in the reactor and the gas flow rate.

5.2.1. Reaction route as a function of temperature

In order to establish the reaction route of the oxidation of Cu_2S a number of experiments was carried out using cups of type I filled with approximately 1 mg of Cu_2S sample to minimize the influence of possible mass transfer limitations. The results of these experiments are given in Figs. 7–10. The experiments carried out using a reaction gas containing 10 vol.% oxygen are shown in Figs. 7 and 8, for 5 vol.% oxygen the results can be found in Figs. 9 and 10. The mass increase found during runs 15 (450 °C) and 16 (550 °C), shown in Fig. 7, confirms the formation of copper sulfate or basic copper sulfate. The mass decrease as found during runs 17 and 18 can be explained by the formation of the intermediate product Cu_2O (and this, thus, shows that Cu_2S is not directly converted into CuO). At a temperature of 550 °C it appeared that the (basic) copper sulfate is eventually converted into copper oxide, as was shown by the sulfur mass balance. These experimental results indicate that at a temperature of 550 °C or higher, CuO is the final product. However, at a temperature of 450 °C the formed copper sulfate does not react further. This is in line with the predominance diagram given in Figs. 2 and 3. When a reaction gas containing 5 vol.% oxygen is applied, the formation of copper sulfate or basic copper sulfate is not found during the experiments performed at temperatures of 550 °C and above. Except for the experiments 15 and 16 (during which (basic) copper sulfate was also formed) the only components present in the sample during these experiments are Cu_2S, Cu_2O and CuO. As a representative example the relative amounts of Cu_2S, Cu_2O and CuO as a function of time present during run 3 are shown in Fig. 11. From Fig. 11 it can be seen that the oxidation of Cu_2S to CuO does not take place in a single reaction step, but that Cu_2S is first converted into Cu_2O, which is then further oxidized to CuO. This reaction path has also been observed by Peretti [5] and Asaki et al. [10]. In Fig. 11 it is also shown that the time during which the reaction takes place can be divided in three separate stages. During stage I, Cu_2S is almost solely converted into Cu_2O and SO_2. Only a small fraction of the Cu_2O formed reacts further to CuO. This means that during this stage of the experiment the rate of the oxygen consumption is almost completely determined by the oxidation of Cu_2S to Cu_2O. During the final stage of the experiment (stage III) virtually all of the Cu_2S has already been converted into Cu_2O. During this stage the reaction responsible for the oxygen consumption is the conversion of Cu_2O into CuO. During stage II both reactions contribute to the rate of oxygen consumption. At temperatures above 650 °C the powdered samples ($38\ \mu m < d_P < 45\ \mu m$) were completely converted in less than approximately 180 s. This is a remarkably short period when compared to the 1–3 h as mentioned in literature for the conversion of Cu_2S in a pelletized shape, Peretti [5], Ramakrishna and Abraham [8], Asaki et al. [10],

indicating mass transfer resistances in the latter case. However, since the influence of the external mass transfer was not determined during this initial set of experiments the present data cannot directly be used to derive kinetic constants. A series of additional experiments using the dedicated type II cups has been carried out to account for the influence of mass transfer on the overall conversion rate.

5.2.2. Reaction rate constant measurement

Since the rate of oxygen consumption during stage I is almost completely determined by the oxidation of Cu_2S to Cu_2O, this rate, which can be derived from the experimental results, may be used to derive the reaction rate. Unfortunately, the reaction rate of the oxidation of Cu_2O to CuO could not be determined the same way from the experimental results, since the observed change in mass due to the oxygen consumption during stage III was too small. In order to determine parameters which influence the reaction rate of the oxidation of Cu_2S to CuO a number of experiments was carried out. In order to allow the mass of the sample to be varied from 1 to 32 mg the type II cups had to be used (see Fig. 5). During these experiments the reaction temperature, the sample mass and the oxygen concentration in the reaction gas were varied. The first step in the oxidation of Cu_2S to CuO is given by the following reaction equation:

$$Cu_2S + \tfrac{3}{2}O_2 \rightarrow Cu_2O + SO_2 \quad (8)$$

From Fig. 11 it can be seen that in the current experiments this step is distinguishable as a separate reaction step and derivation of the kinetics is possible if the following phenomena are properly accounted for:

1. the diffusion of oxygen towards the sample cup;
2. the diffusion of oxygen within the sample bed;
3. the diffusion of oxygen within the sample particles;
4. the chemical reaction (this is the actual kinetics);
5. the diffusion of the formed sulfur dioxide within the sample particles;
6. the diffusion of the formed sulfur dioxide through the sample bed;
7. the diffusion of sulfur dioxide from the sample cup.

Since the oxidation of Cu_2S to Cu_2O may be considered to be irreversible (see Table 1), only steps 1–4 can be influencing the conversion rate. When the reaction between oxygen and Cu_2S is described using a simple power law rate equation and is considered to be *n*th order in oxygen, the rate at which this reaction proceeds can be calculated using Eq. (16):

$$R\,(\mathrm{mol\,Cu_2S\,s^{-1}}) = k_{app} C_{O_2}^{n} m \quad (16)$$

The corresponding oxygen demand of the reaction can be determined from the reaction stiochiometry. Taking diffusion resistances into account the overall oxygen consumption can now be expressed as

$$N_{O_2} = \frac{1}{(1/k_{diff} A C_{O_2}) + (1/v k_{app} C_{O_2}^{n} m)} \quad (17)$$

In Eq. (17) k_{diff} is a mass transfer coefficient in which all diffusion mass transfer resistances not directly related to the amount of sample are lumped.

5.2.3. Experimental results

In stage I, the oxidation of Cu_2S to Cu_2O is predominant, and the oxygen consumption rate has been solely attributed to this reaction. By varying the amount of the sample and plotting the oxygen consumption rate *N* as a function of the sample mass m both the parameters k_{diff} and k_{app} can be obtained from the experimental data. A representative example of such a plot is given in Fig. 12. It can be seen that at high sample masses the mass transfer rate at which oxygen can

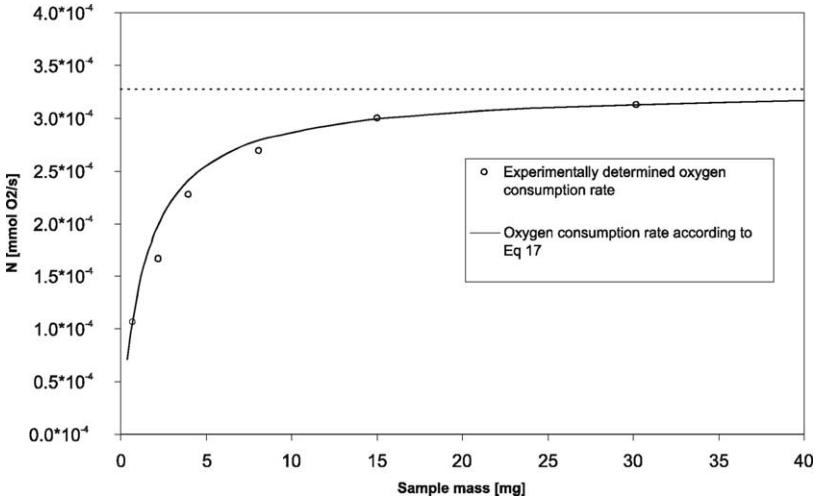

Fig. 12. The experimentally determined oxygen consumption rate as a function of the sample mass at a $T = 650\,^{\circ}C$ and $C_{O_2} = 5$ vol.% and the oxygen consumption rate according to Eq. (17), with a k_{diff} of 5.03×10^{-7} $m^3\,s^{-1}$ and a k_{app} of 2.27×10^{-1} mol $kg^{-1}\,s^{-1}$. The dashed line shows the reaction rate for a completely mass transfer limited process.

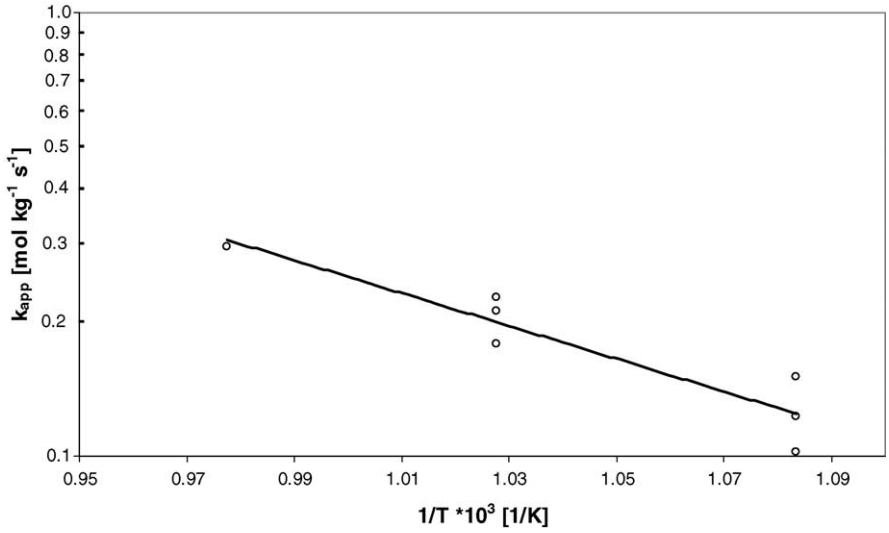

Fig. 13. Arrhenius plot for reaction (9).

be transported towards the reaction zone, either externally or internally, becomes rate determining. At low sample masses the overall rate becomes dependent on the mass of the sample also, so both the mass transfer process and the chemical reaction rate determine the oxygen consumption rate. The fraction of the overall resistance that can be ascribed to the mass transfer resistance increases with increasing sample mass; at sample masses of 4 and 32 mg mass transfer contributes 73 and 95% to the overall resistance, respectively. The experiments carried out were split in several series, each carried out at the same temperature and oxygen concentration. The value of k_{diff} has been determined for all experimental series by determining the height of the dashed plateau as shown in Fig. 12. With the overall mass transfer resistance known from the plateau, the apparent reaction rate constant can be estimated for each experiment that is not (completely) determined by mass transfer. From the, thus, obtained apparent kinetics the reaction appeared to be of zeroth order in oxygen. The obtained apparent reaction rate constants are plotted in the Arrhenius plot given in Fig. 13. The obtained relationship can be expressed by Eq. (18) given in Table 3. The activation energy found for this oxidation reaction is 71 kJ/mol. The order of magnitude of the activation energy confirms that the conversion is not limited by a diffusion process, which generally displays a substantially lower activation energy than a chemical reaction. In Fig. 14 a parity plot is given in which the oxygen consumption rate as obtained from the experimental results is plotted versus the oxygen consumption rate

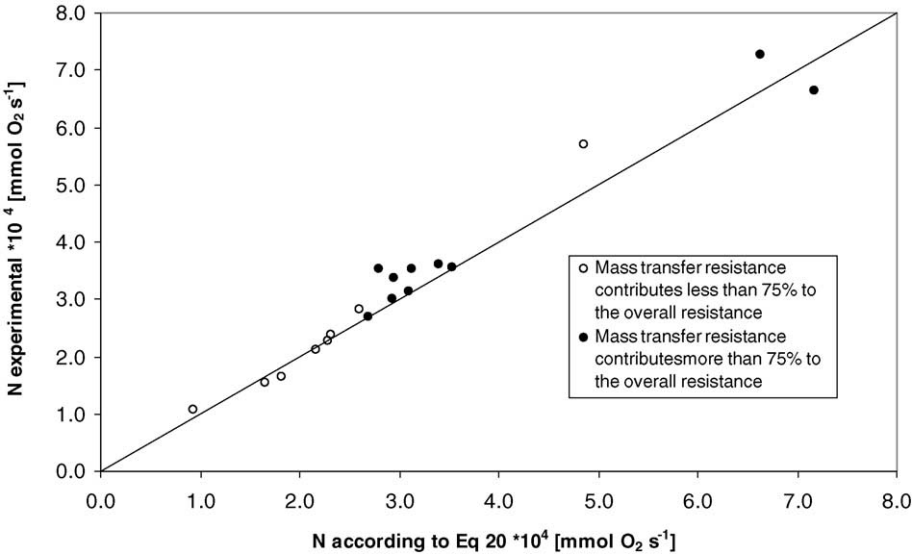

Fig. 14. Experimental oxygen consumption rate vs. oxygen consumption rate according to Eq. (17), for all Cu_2S oxidation experiments carried out using type II Quartz cups.

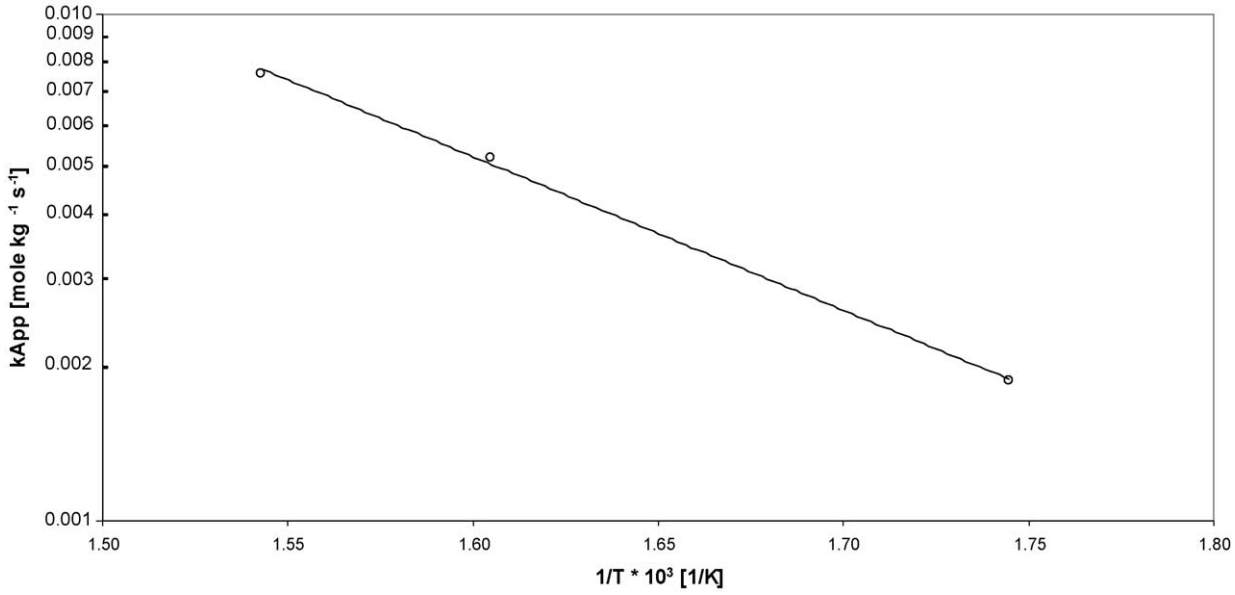

Fig. A1. k_{app} for the reaction of CuS to Cu_2S as a function of temperature. The sample mass was 32 mg and the oxygen concentration of 5 vol.%.

derived from Eqs. (17) and (18) for all experiments carried out using type II cups. It can be seen that the agreement is generally within 10%.

5.3. Diffusion processes

A comparison of the experimentally determined values of the mass transfer coefficients and the values of the mass transfer coefficients according to the relations mentioned in literature has been made. It appeared that not internal mass transfer (sample bed diffusion, estimated according to Bischoff [13]), but external mass transfer is (partially) rate limiting at the experimental conditions applied. Furthermore, it appeared that the experimentally determined values for the external mass transfer coefficient k_{diff} agree reasonably well (within 20%) with the values obtained using the well-known theoretical Ranz–Marshall relation (Eq. (20)) as given by Ranz and Marshall [14]:

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/3} \quad (20)$$

5.4. Heat effects

The influence of the reaction heat generated during the oxidation of Cu_2S to Cu_2O on the temperature of the sample has been estimated using the method described by Szekely et al. [15]. A worst case estimate learns that the temperature of the sample was never more than 15 °C higher than the temperature of its surroundings. Therefore, it can be concluded that the influence of the heat effects on the experimental results is limited.

Table 3
The oxidation of Cu_2S to Cu_2O

	Eq. no.	Equation
Oxidation reaction		$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2$
Rate expression (mol Cu_2S s^{-1})	(18)	$R = k_{app} m C^0_{O_2}$
Reaction rate constant (mol kg^{-1} s^{-1})	(19)	$k_{app} = 1.28 \times 10^3\, e^{-71.103/RT}$

6. Conclusions

In the current study the oxidation of CuS to CuO at temperatures in the range of 450–750 °C and oxygen concentration as encountered during roasting (5–10 vol.%) has been studied experimentally using a thermogravimetric analyzer. Thermodynamics show that the formation of CuO from CuS is possible if the SO_2 partial pressure is sufficiently low. Besides CuO some by- or intermediate products like (basic) copper sulfate or Cu_2O may be formed during the oxidation of CuS. The stability of these byproducts depends on the process conditions like temperature, sulfur dioxide and oxygen concentration. At temperatures up to 527 °C (basic) copper sulfate is a stable component. Experiments have shown that the oxidation of CuS to CuO consists of several reaction steps, the conversion of CuS to Cu_2S being always the first step. Since this reaction appeared to be a fast reaction compared to the other reactions that may occur, Cu_2S was chosen as starting material for the oxidation experiments carried out at temperatures above 400 °C (above this temperature CuS reacts very fast to Cu_2S both in the presence and absence of oxygen). The experimental results showed that the time needed for a complete conversion of the copper sulfide to copper oxide was very short when compared to the reaction times mentioned in literature. At temperatures above 650 °C the powdered Cu_2S samples were completely converted to

CuO in less than approximately 3 min as compared to the 1–3 h reaction time typically mentioned in literature for the conversion of Cu_2S in a pelletized shape. The experimental results showed that at temperatures up to 550 °C CuS and Cu_2S may be converted (partially) into (basic) copper sulfate. Above this temperature it is possible to convert Cu_2S selectively and completely to CuO. The oxidation of Cu_2S to CuO appeared to be a two step process. The first reaction step is the oxidation of Cu_2S to Cu_2O. The second step is the subsequent oxidation of Cu_2O to CuO. The rate at which Cu_2S is converted into Cu_2O increased with temperature. Both chemical reaction and mass transfer influenced the conversion rate. To derive the intrinsic kinetics from the experimental results a number of experiments were performed in which the temperature and amount of sample used were varied. The kinetics of the oxidation reaction of Cu_2S to Cu_2O have thus been determined as a function of temperature (Table 3).

It was not possible to determine the kinetics for the subsequent oxidation of Cu_2O to CuO because of the limited weight change during this reaction step, but the reaction rate seems to be of the same order of magnitude as for the reaction of Cu_2S to Cu_2O. It can be concluded that the current experimental results demonstrate that a conversion of copper sulfide to copper oxide, preventing the formation of by-products is possible at temperatures in the range of 550–750 °C, oxygen concentrations of 5–10% and that the required contact time is in the order of minutes.

Appendix A. Decomposition of CuS in the presence of O_2

Peretti [5] and Ganguly and Mukherjee [7] have reported that the first reaction step in the oxidation of CuS is the fast decomposition of CuS to Cu_2S. The rate at which the reaction of CuS to Cu_2S takes place depends on the presence of oxygen in the reaction gas, which enhances the decomposition rate considerably. A number of 16 experiments have been performed to study the decomposition rate of CuS to Cu_2S. The temperature during these experiments was varied between 300 and 750 °C. However, due to the high reaction rate at the higher temperatures, only the experiments carried out at temperatures between 300 and 375 °C were interpretable. Experiments were carried out using a nitrogen/air mixture containing 5 vol.% oxygen as reactor feed gas.

It appeared that the conversion of CuS in the presence of oxygen at a constant temperature is a two stage process. First, CuS decomposes into Cu_2S and elemental sulfur, which is subsequently oxidized to SO_2 (shown as Eqs. (A.1) and (A.2)). Only after all CuS is converted to Cu_2S, the formed Cu_2S is oxidized further to, in this case (basic) copper sulfate (Eq. (A.3)):

$$2x\mathrm{CuS} \rightarrow \mathrm{Cu_2S} + \mathrm{S}_x \quad \text{(A.1)}$$

$$\mathrm{S}_x + x\mathrm{O_2} \rightarrow x\mathrm{SO_2} \quad \text{(A.2)}$$

$$\mathrm{CuS} + \tfrac{5}{2}\mathrm{O_2} \rightarrow \mathrm{CuO \cdot CuSO_4} \quad \text{(A.3)}$$

The formation of (basic) copper sulfate was due to the low temperatures (see also Figs. 6 and 7 in the main text). It appeared that the observed reaction rate of the conversion of CuS to Cu_2S increased with temperature. Using the data available and the same procedure as used in Section 5.2.2, an estimate of the apparent reaction rate constant of reaction (A.1) was made. Since the concentration of oxygen was not varied during these experiments the reaction order in oxygen could not be determined and the reaction between oxygen and CuS is described using a simple rate equation (Eq. (A.4)) in which the oxygen effect is implemented in k_{app}:

$$R\,(\mathrm{mol\,CuS\,s^{-1}}) = k_{app} m \quad \text{(A.4)}$$

By lack of experimental data on the mass transfer coefficient, the external mass transfer coefficient was estimated using the Ranz–Marshall equation [14]. The obtained apparent reaction rate constants are shown in Fig. A1. The obtained Arrhenius relationship can be expressed by Eq. (A.5):

$$k_{app} = 3.76 \times 10^3\, \mathrm{e}^{-58\times10^3/RT} \quad \text{(A.5)}$$

The activation energy found for this oxidation reaction was 58 kJ/mol. The order of magnitude of the activation energy as found in this study indicates that the reaction rate is again most probably not limited by a diffusion process, which generally displays a substantially lower activation energy than chemical kinetics. The obtained value of the reaction rate constant and the increase of the reaction rate as a function of temperature indicate that the conversion of CuS to Cu_2S, at higher temperatures, cannot be a rate determining step in the overall oxidation of CuS to CuO. This also means it is justified to use Cu_2S as starting material for the oxidation experiments in this study.

References

[1] A.L. Kohl, R.B. Nielsen, Gas Purification, Gulf Publishing Co., Houston, 1997.
[2] R.R. Broekhuis, D.J. Koch, S. Lynn, A medium temperature process for removal of hydrogen sulfide from sour gas streams with aqueous metal sulfate solutions, Ind. Eng. Chem. Res. 31 (1992) 2635–2642.
[3] H. ter Maat, G.F. Versteeg, Method and system for selective removal of contamination for gas flows. European Patent EP19980925979 (1997).
[4] H. ter Maat, J.A. Hogendoorn, G.F. Versteeg, The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent. Part I. The absorption of hydrogen sulfide in metal sulfate solutions, Sep. Purif. Technol., in press.
[5] E.A. Peretti, A new method for studying the mechanism of roasting reactions, Disc. Faraday Soc. 4 (1948) 174–179.
[6] J.R. Lewis, J.H. Hamilton, J.C. Nixon, C.L. Graversen, The oxidation of chalcocite in air compared with its oxidation in pure oxygen, TMS–AIME 182 (1949) 177–185.
[7] N.D. Ganguly, S.K. Mukherjee, Studies on the mechanism and kinetic of the oxidation of copper sulphide, Chem. Eng. Sci. 22 (1967) 1091–1105.

[8] V.V.V.N.S. Ramakrishna Rao, K.P. Abraham, Kinetics of oxidation of copper sulfide, Met. Trans. 2 (1971) 2463–2470.
[9] E. Açma, C. Oktaybas, H. Sesigür, O. Addemir, Benification of Divrigi tailings by flotation, sulfatizing roasting, leaching and H_2S precipitation, Erzmetall 58 (1995) 572–577.
[10] Z. Asaki, A. Ueguchi, T. Tanabe, Y. Kondo, Oxidation of Cu_2S pellet, Trans. Jpn. Instit. Met. 27 (1986) 361–371.
[11] I. Barin, Thermochemical Data of Pure Substances, VCH, Weinheim, 1993.
[12] U.H.F. Sander, H. Fischer, U. Rother, A.I. More, Sulphur, sulphur dioxide and sulphuric acid: an introduction to their industrial chemistry and technology, British Sulphur Corporation, 1984.
[13] K.B. Bischoff, Effectiveness factor for general reaction rate forms, AICHE J. 11 (1965) 351.
[14] W.E. Ranz, W.R. Marshall Jr., Evaporation from drops, part II, Chem. Eng. Progr. 48 (1952) 173–180.
[15] S. Szekely, J.W. Evans, H.Y. Sohn, Gas–Solid Reactions, Academic Press, 1976.